GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 9/10/80

Project Title: NEW REAGENTS AND NEW REACTIONS IN ORGANOMETALLIC CHEMISTRY

Project No: G-33-668

Project Director: DR. E. C. ASHBY

Sponsor: AMERICAN CHEMICAL SOCIETY-PETROLEUM RESEARCH FUND

Agreement Period: From 9/1/80 Until 8/31/82

Type Agreement: PRF GRANT #12545 - AC1

Amount: $30,000

Reports Required: COMPREHENSIVE REPORTS AT LEAST ONCE EACH YEAR.

Sponsor Contact Person (s):

Technical Matters

Contractual Matters
(thru OCA)

JUSTIN W. COLLAT
PROGRAM ADMINISTRATOR
AMERICAN CHEMICAL SOCIETY
THE PETROLEUM RESEARCH FUND
1155 SIXTEENTH STREET, N.W.
WASHINGTON, D.C. 20036
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Defense Priority Rating: NONE

Assigned to: CHEMISTRY (School/Laboratory)

COPIES TO:

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 2/14/83

Project Title: New Reagents & New Reactions in Organometallic Chemistry

Project No: G-33-668

Project Director: Dr. E. C. Ashby

Sponsor: American Chemical Society, The Petroleum Research Fund

Effective Termination Date: 8/31/82

Clearance of Accounting Charges: 8/31/82

Grant/Contract Closeout Actions Remaining:

- [x] Final Invoice and Closing Documents
- [x] Final Fiscal Report Filed 2/8/83
- [x] Final Report of Inventions (If positive)
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Assigned to: Chemistry (School/~~Laboratory~~)

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THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 12545 ACI

Page 1 of 1 pages.

PREPARED BY

E. C. Ashby

Date September 16, 1981

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

12545-ACI Single Electron Transfer in Organic Reactions

E.C. Ashby, Georgia Institute of Technology

Progress during the past year centers around two areas of endeavor: (1) Evidence for Single Electron Transfer (SET) in reactions of lithium tetra-(N-dihydropyridyl)aluminate (LDPA) with various organic functional compounds and (2) Evidence for SET in reactions of lithium dialkylcuprates ($LiCuR_2$) with alkyl halides

LDPA was first prepared by Landsbury[1] by the reaction of $LiAlH_4$ with pyridine. This compound was shown to have unusual reducing capability although little is known about its mechanisms of reaction. We have shown that blue colored, esr active solutions were produced when LDPA was allowed to react with dimesityl ketone (DMK) or mesitylphenyl ketone (MPK). Both the intensity of the esr signals as well as the visible absorption spectra increased with time at the same rate in a particular reaction indicating that both the color and the esr signals are due to the same species. After a period of time the esr signal decreased in intensity as the product formed. Mechanistic studies indicate the formation of a radical anion (ketyl) and radical cation followed by hydrogen atom abstraction to form the reduction product. Reactions of LDPA with several polynuclear hydrocarbons also exhibited the presence of SET by identification of radical anion intermediates. Additionally, reactions of LDPA with trityl halides showed the intermediate formation of the trityl radical ($Ph_3C\cdot$).

Studies in progress concerning the reactions of $LiCu(CH_3)_2$ and other alkyl cuprates with trityl halides also show the intermediate formation of the trityl radical. Evidence of SET in the reaction of cuprates with hexenyl iodide probes involves the observation of cyclized products indicating the existence of a radical intermediate.

(1) P.T. Landsbury, J. Amer. Chem. Soc., (1961) 83, 429.